

# PURIFICATION AND CHARACTERIZATION OF METHYL PHTHALYL ETHYL GLYCOLATE (MPEG)

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*and*

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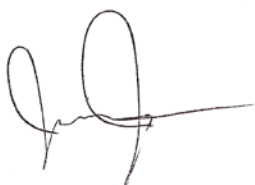
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## FOREWORD

The analytical work described herein helps address some of the propellant manufacturing issues for HES 5808 propellant, which is used for Cartridge Actuated Device and Propellant Actuated Device (CAD-PAD) applications. Methyl phthalyl ethyl glycolate (MPEG) is the inert plasticizer used for this propellant, and poor propellant manufacturing has been attributed to the variable quality of lots of MPEG procured from outside vendors. The ability to assess the quality of various lots of MPEG, and its effect on the physical properties of MPEG, is required so that HES 5808 and other formulations containing MPEG can be reliably manufactured.



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**LIST OF ABBREVIATIONS AND ACRONYMS**

ASTM	American Society for Testing and Materials
BHT	Butylated hydroxytoluene
CAD-PAD	Cartridge Actuated Device and Propellant Actuated Device
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EA	Elemental analysis
Et <sub>3</sub> N	Triethylamine
Et <sub>2</sub> O	Diethyl ether
IR	Infrared spectroscopy
GC	Capillary gas chromatography
GC-MS	Capillary gas chromatography mass spectroscopy
HES	Hercules Experimental Smokeless
HRMS	High resolution mass spectroscopy
KF	Karl Fischer analysis
MeOH	Methanol
MgSO <sub>4</sub>	Magnesium sulfate
MPEG	Methyl phthalyl ethyl glycolate
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance spectroscopy
R <sub>f</sub>	Retention factor
TLC	Thin layer chromatography
UV-Vis	Ultraviolet visible spectroscopy



## ABSTRACT

We report the purification of methyl phthalyl ethyl glycolate (MPEG) by flash column chromatography (ca. grams), allowing us to establish an analytically pure standard using EA, KF, GC, and GC-MS analyses. The purified MPEG was fully characterized using  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, UV-Vis, bp, and HRMS analyses. Using this standard, routine GC analysis can be performed to determine the purity with a high degree of confidence of various lots of MPEG, improving the quality control for formulations containing MPEG.

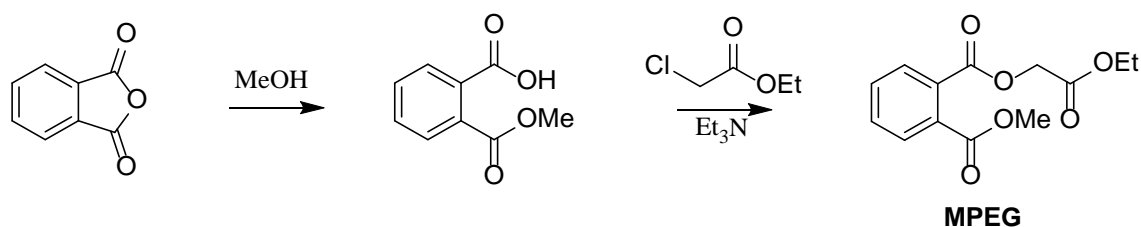
## INTRODUCTION

Methyl phthalyl ethyl glycolate (MPEG) has been a commercially available plasticizer since at least 1942 (Van Antwerpen, **1942**), known then as Santicizer M-17 by the Monsanto Chemical Company. MPEG is used in HES 5808, a high solids-loading propellant composed of two solids: cellulose acetate and ammonium perchlorate. MPEG is added, along with three processing solvents (acetone, ethanol, and either butyl acetate or ethyl lactate), to plasticize the cellulose acetate. Poor propellant manufacturing, which can produce unacceptable propellant grains, has been attributed to the inconsistent quality of MPEG, and sufficient anecdotal evidence exists that MPEG viscosity and aging characteristics vary from lot to lot. This situation has emerged since Monsanto no longer produces MPEG, and alternative vendors are currently being used and evaluated. Thus, the minimum purity of MPEG required and the acceptable values for its physical properties (e.g., viscosity, surface tension) for HES 5808 propellant manufacturing remain undetermined. Also, acceptable storage conditions for MPEG remain undetermined.

## BACKGROUND

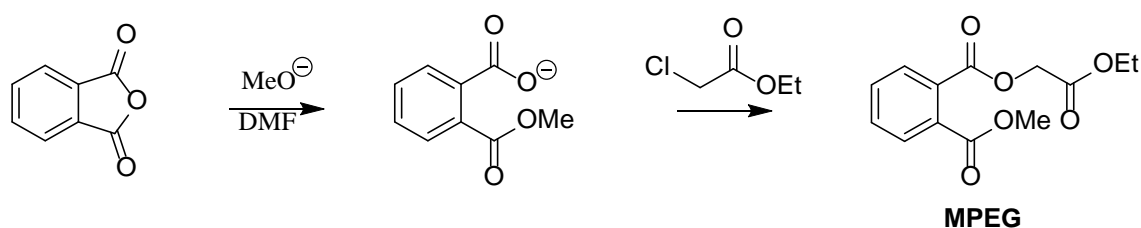
MPEG has never been completely characterized. Indeed, only the boiling point (Van Antwerpen, **1942**), specific gravity (Van Antwerpen, **1942**), refractive index (Whitnack and Gantz, **1953**), viscosity (Ladner and Becker, **1965**), and gas chromatography (Krishen, **1971**) have been reported in the open literature. Furthermore, the purity of MPEG has not been established. Although MPEG is known to be a clear, viscous liquid (Van Antwerpen, **1942**), various commercial lots have displayed a slightly yellowish or amber color. Moreover, a milky-white precipitate would occasionally form in some of these lots over time.

The Monsanto process to synthesize MPEG uses phthalic anhydride and methanol in the first step, and this reaction mixture is heated to 60 °C (Monsanto, **1963**). After the addition of triethylamine and ethyl chloroacetate in the second step, the reaction mixture is heated to 130 °C (Fig. 1). The simple workup involves washings with acid and then water to yield a colorless oil.



**Figure 1.** Monsanto method of MPEG synthesis

The Incon process uses phthalic anhydride and sodium methoxide in dimethylformamide (DMF) in the first reaction step. Ethyl chloroacetate is added in the second reaction step, and the reaction mixture is heated to 120 °C. At the end of the reaction, the DMF is removed via vacuum distillation (Fig. 2). Incon Industries and the Chemical Development Branch at NSWC IHEODTD have used this method, producing variable quality MPEG. An analytically pure standard was needed to quantify the purity of these lots.



**Figure 2.** Incon method of MPEG synthesis

## RESULTS

Our initial attempts to purify Incon MPEG that contained floating solids included vacuum filtration and then successive base washings using a separatory funnel. However, neither vacuum filtration nor base washing significantly improved the purity. These failed attempts to purify Incon MPEG by aqueous and alkaline washes eliminate the possibility that the main impurity was a neutral salt or an acid.

We then attempted to purify Incon MPEG by vacuum distillation at 5 Torr since MPEG was reported to boil at 189 °C at this pressure (Van Antwerpen, **1942**). However, we were unable to vacuum distill MPEG at pressures even lower than 0.5 Torr. MPEG decomposition may have occurred, as the contents of the distillation flask irreversibly changed color from slightly yellow to red; MPEG decomposition under vacuum distillation has been previously noted, occurring at 200 °C (Ladner and Becker, **1965**).

### Purification of City Chemical MPEG

We successfully purified MPEG that had been synthesized by City Chemical, via flash column chromatography using silica gel and diethyl ether. We dried the purified MPEG over sodium sulfate and removed volatile solvents from the viscous oil under high vacuum. The purified MPEG was stored in a refrigerator under Argon.

### Purity Characterization

We established the purity of the MPEG standard using elemental analysis (EA), capillary gas chromatography (GC), and Karl Fischer analysis (KF). EA determined that the MPEG standard was analytically pure, as triplicate measurements of carbon, hydrogen, and oxygen were within 0.4 mass percent of theory. GC determined the purity of the MPEG standard to be 99.5 mass percent, using duplicate measurements of the relative ion count ratio between MPEG at 14.1 min and the one other measurable impurity at 13.25 min. KF determined the water content of the MPEG standard to be less than 0.3 mass percent.

### Structure Characterization

We established the structure of the MPEG standard using proton and carbon nuclear magnetic resonance spectroscopy ( $^1\text{H}$  and  $^{13}\text{C}$  NMR), high resolution mass spectroscopy (HRMS), capillary gas chromatography mass spectroscopy (GC-MS), infrared spectroscopy (IR), ultraviolet visible spectroscopy (UV-Vis), and boiling point determination (bp).

$^1\text{H}$  NMR analysis of the MPEG standard is consistent with its structure: a) four aromatic protons (7.84-7.71 ppm) whose splitting pattern suggests a 1,2-asymmetrically disubstituted benzene ring; b) two uncoupled methylene protons (4.90 ppm) significantly shifted downfield; c) five protons (4.19 and 1.23 ppm) for the ethyl group; and d) three protons (3.81 ppm) for the methyl group. The other observed resonances are either  $^{13}\text{C}$  satellite peaks, which are symmetrical about a chemical shift of MPEG, or trace impurities.

$^{13}\text{C}$  NMR analysis of the MPEG standard is also consistent with its structure. Two of the three carbonyl resonances observed (167.3 and 167.2 ppm) nearly co-resonate, suggesting that these two carbonyls possess very similar magnetic environments, which is consistent with the  $^1\text{H}$  NMR splitting pattern in the aromatic region of a 1,2-asymmetrically disubstituted benzene ring. Note, these two carbonyls will appear as one observed chemical shift if an unmatched exponential filter is used (i.e., a line broadening of 5.0 Hz is used instead of 0.3 Hz). Thus the other carbonyl resonance (166.0 ppm) can be assigned to the glycolate ester. Six aromatic resonances (132.2, 131.9, 131.5, 130.0, 128.9, and 128.7 ppm) and four alkyl resonances (61.6, 60.9, 52.5, and 13.9 ppm) are observed, for a total of thirteen observed carbon resonances. No other resonances are observed.

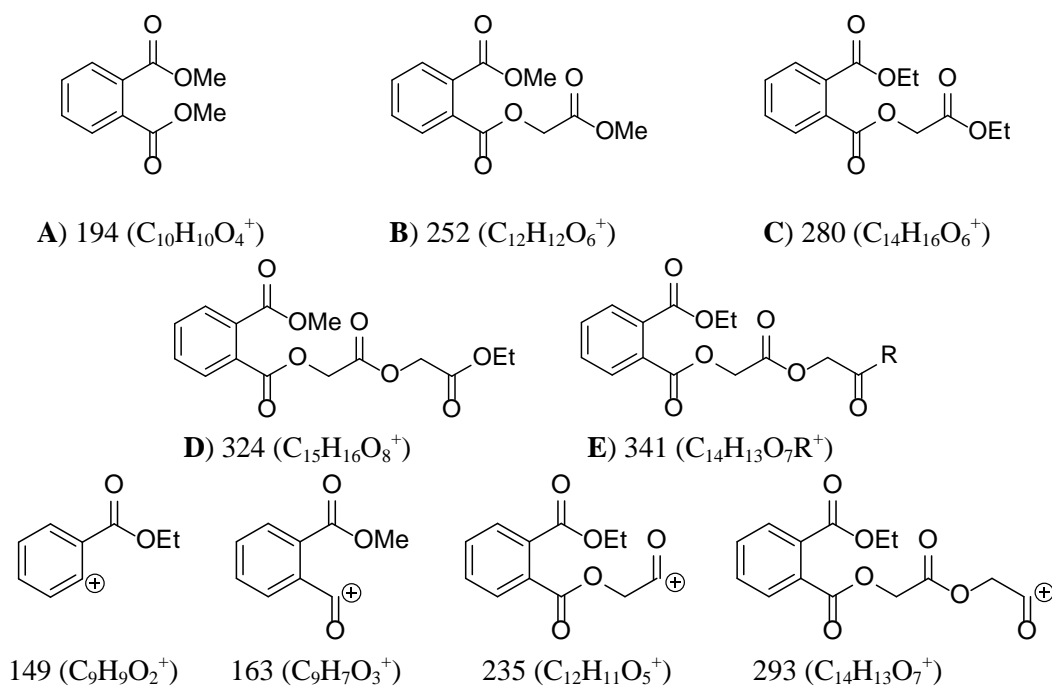
GC can resolve seven peaks in the chromatogram of the MPEG standard. GC-MS analysis of the seven peaks shows the parent ions as radical cations in low mass resolution with significant fragmentation (Table 1). MPEG is the predominant peak in the chromatogram and its parent mass ion, 266 ( $\text{M}^+$ ), and its major fragmentation ion, 163, are observed in the mass spectrum. The parent mass ion of butylated hydroxytoluene (BHT), an antioxidant present in diethyl ether, is observed and its fragmentation ion pattern strongly matches the known spectra in the NIST database. The five remaining compounds (**A-E**) are present in less than 1 percent combined, and each appears to be a phthalyl derivative based on their parent mass ion and fragmentation pattern (Fig. 3). Indeed, the fragmentation ion pattern of **C** strongly matches the known spectrum in the NIST database, and we propose phthalate structures for **A**, **B**, **D**, and **E** as well. Supporting our structural assignments for **B** and **C** are their close retention times to MPEG. Supporting our structural assignments for **A** and **D** is mass fragment 163, indicating a methyl phthalyl derivative as observed in the fragmentation pattern of **B** and MPEG. We have not determined a complete structural assignment for **E**, and we suspect that the parent mass ion of **E** is greater than 341. However, supporting our structural assignments for **E** are mass fragments 149 and 235, indicating an ethyl phthalyl glycolyl derivative as both these ions are observed in the fragmentation pattern of **C**, and mass fragment 293, which indicates an ethyl phthalyl glycolyl-glycolyl derivative observed in the fragmentation pattern of **D**.

HRMS analysis of the MPEG standard shows the parent mass ion, 267 ( $\text{M}+\text{H}^+$ ), in high mass resolution with a high signal-to-noise ratio. Two other mass ions (163 and 235) are also observed, and are presumed to be the same fragmentation ions observed using GC-MS since mass ion 163 is high mass resolution for  $\text{C}_9\text{H}_7\text{O}_3$  and mass ion 235 is high mass resolution for  $\text{C}_{12}\text{H}_{11}\text{O}_5$ . Because HRMS uses much softer ionization conditions than GC-MS, extensive fragmentation is often not observed and the parent mass ion can be readily identified in its protonated form ( $\text{M}+\text{H}^+$ ). The high resolution determination of the HRMS fragmentation ions strengthens the GC-MS analysis as one of these ions is observed in every one of the spectra for compounds **A-E**.

**Table 1.** GC-MS Analysis of the MPEG Standard

#	GC-MS (min)	GC (min)	Parent Ion (m/z)	Fragment Ions (m/z)	Identity
A	7.294	8.595	194	163	Dimethyl phthalate
	7.955	9.356	220	205	BHT
B	11.350	13.250	252	163	Methyl phthalyl methyl glycolate
	12.109	14.075	266	163, 235	MPEG
C	12.883	14.593	280	149, 235	Ethyl phthalyl ethyl glycolate
D	15.381	17.382	324	163, 293	Methyl phthalyl ethyl glycolyl glycolate
E	15.766	17.809	341*	149, 235, 293	<i>ethyl phthalyl glycolyl-glycolyl derivative</i>

\* Highest mass ion observed; may not be the parent ion

**Figure 3.** Possible structures for the mass ions observed in GC-MS

IR analysis of the MPEG standard confirms the presence of an ester linkage. The strong absorption band assigned to the ester carbonyl stretch ( $1728\text{ cm}^{-1}$ ) is consistent for a benzoate ester, whose C=O stretches are observed between 1715 and 1730 wavenumbers (Silverstein et al., **1991**; Pretsch et al., **2000**). The corresponding ester C-O stretching vibrations ( $1286$ ,  $1210$ ,  $1124$ , and  $1080\text{ cm}^{-1}$ ) are also observed. UV-Vis analysis of the MPEG standard confirmed the presence of an aromatic ring, showing a strong extinction coefficient (ethanol) at a maximum absorption wavelength ( $272\text{ nm}$ ) in the ultraviolet region.

Vacuum distillation of the MPEG standard determined the boiling point at vacuum pressures lower than previously reported (bp =  $137\text{ }^{\circ}\text{C}$  at  $0.10\text{ Torr}$ ). The MPEG standard cleanly distilled over, and impurities were not detected in the colorless distillate by  $^1\text{H}$  NMR.

### Purification of Incon MPEG

We successfully purified MPEG that had been synthesized by Incon, via flash column chromatography using silica gel and diethyl ether. In addition, we were able to isolate and characterize a major impurity in this Incon lot. EA determined that this Incon purified MPEG was not quite analytically pure; although duplicate measurements of both carbon and hydrogen were within 0.4 mass percent of theory, EA for oxygen was not. KF determined the water content to be less than 0.25 mass percent. The aromatic region of the  $^1\text{H}$  NMR spectrum for the Incon purified MPEG remains a complicated multiplet, yet does appear to be different than the unpurified material. However, the  $^{13}\text{C}$  NMR spectrum is clearly different, as traces of impurities are observed.

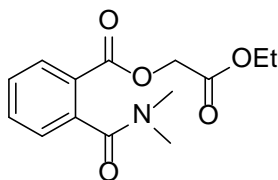
### Column Impurity

We successfully isolated and characterized a major impurity in the Incon lot via flash column chromatography using silica gel and diethyl ether. Thin layer chromatography (TLC) shows an ultraviolet active spot with a lower retention factor ( $R_f$ ) than MPEG, strongly suggesting a more polar, neutral compound than MPEG. We can conclude that this column-isolated impurity is not a salt because its  $R_f$  value is not zero in a nonpolar solvent (diethyl ether), which is consistent with our previous failed attempts to purify the Incon MPEG by aqueous washings.

$^1\text{H}$  and  $^{13}\text{C}$  NMR analysis of the column-isolated impurity clearly establishes a structure very similar to MPEG. The  $^1\text{H}$  NMR spectrum shows a) four discrete (not a multiplet) aromatic protons whose splitting pattern suggests a 1,2-asymmetrically disubstituted benzene ring; b) two uncoupled methylene protons significantly shifted downfield; c) five protons for the ethyl group; and d) six protons for two methyl groups. The only differences between the  $^1\text{H}$  NMR spectra of MPEG and the column-isolated impurity are that a) the methyl ester singlet of MPEG has disappeared; and b) two new methyl singlets of the column-isolated impurity appear.

The  $^{13}\text{C}$  NMR analysis of the column-isolated impurity shows fourteen carbons instead of the thirteen for MPEG. This  $^{13}\text{C}$  NMR spectrum shows a) three carbonyl carbons that are distinctly observed; b) six aromatic carbons; and c) five alkyl carbons. The only differences between the  $^{13}\text{C}$  NMR spectra of MPEG and the column-isolated impurity are that a) unlike the three MPEG carbonyl carbons, none of the three carbonyl carbons of the column-isolated impurity nearly co-resonate with each other, which is consistent with the  $^1\text{H}$  NMR analysis that the methyl ester is no longer present; and b) an additional alkyl carbon is present in the column-isolated impurity.

HRMS analysis of the column-isolated impurity shows the parent mass ion, 280 ( $\text{M}+\text{H}^+$ ), which is high resolution for  $\text{C}_{14}\text{H}_{18}\text{N}_1\text{O}_5$ . IR analysis of the column-isolated impurity shows two carbonyl absorptions bands. The strong absorption band assigned to the ester carbonyl stretch ( $1726\text{ cm}^{-1}$ ) is consistent for a benzoate ester, whose  $\text{C}=\text{O}$  stretches are observed between 1715 and 1730 wavenumbers, and the strong absorption band assigned to the amide carbonyl stretch ( $1638\text{ cm}^{-1}$ ) is consistent for a tertiary amide, whose  $\text{C}=\text{O}$  stretches are observed between 1630 and 1680 wavenumbers (Silverstein et al., **1991**; Pretsch et al., **2000**). Thus, the column-isolated impurity is an MPEG analog: ethyl glycolyl dimethylphthalamate, a compound unknown in the literature.<sup>1</sup> TLC,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and HRMS analyses are all consistent with the structure for this phthalamate (Fig. 4).



**Figure 4.** Structure of the column-isolated impurity

### Vacuum-Filtered Impurity

We successfully isolated a major impurity in the same Incon lot via vacuum filtration as a white, waxy solid.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis determined the milky-white precipitate to be mostly MPEG, mixed with either the column-isolated impurity or some other unidentified, close analog of dimethylphthalamate, or perhaps even both.  $^1\text{H}$  NMR analysis of the minor component clearly shows two methyl singlets, consistent with the dimethylamide portion of a dimethylphthalamate. Whereas the aromatic region in the  $^1\text{H}$  NMR spectrum of the minor component is difficult to distinguish, the  $^{13}\text{C}$  NMR spectrum of the minor component clearly shows at least 6 aromatic carbons. However, vacuum filtration of this precipitate only marginally improves the purity of the Incon lot.

1) SciFinder Search was conducted on October 31, 2014.

## DISCUSSION

We were able to purify MPEG via flash column chromatography, from both high and low purity lots using the same technique. The high purity lot (City Chemical) had been recently procured in the last year, and then stored in a refrigerator under Argon. The low purity lot (Incon) had been procured sometime earlier, perhaps ten years ago, and stored under dubious conditions. It remains unclear to what extent aging had compromised the Incon lot.

Remarkably, we achieved good separation with a high  $R_f$  value ( $R_f = 0.63$ ) using diethyl ether; column separation can become difficult at  $R_f$  values higher than 0.4 (Gordon and Ford, **1972**). Using a hexane-ethyl acetate solvent system, it may prove possible to improve separation, though MPEG is only slightly soluble in hexane.<sup>2</sup> We were concerned with the possible susceptibility of MPEG to acid-mediated hydrolysis or decomposition, which can occur on silica gel columns for acid-sensitive compounds (Pirrung, **2007**), and we accepted a higher  $R_f$  value. For similar reasons, we decided to use sodium sulfate, instead of the more acidic magnesium sulfate (Pirrung, **2007**), to dry the diethyl ether solution of MPEG. However, our mass recovery using flash column chromatography was very high, so our concerns of MPEG undergoing acid-mediated hydrolysis may be exaggerated. We also chose diethyl ether as an eluting solvent to more fully remove it under high vacuum from the viscous MPEG, as opposed to the less volatile ethyl acetate, in order to pass EA.

As a result of these efforts, routine analysis to quantify MPEG purity can be performed using GC with a high degree of confidence, calibrated against our MPEG standard. Indeed, ASTM method D3465 recommends the use of an internal standard for purities less than 99 mass percent. MPEG impurities are easier to detect using GC and GC-MS than other analytical techniques, such as  $^1\text{H}$  and  $^{13}\text{C}$  NMR. EA may not be a reliable method for routine analysis of MPEG since many of these impurities are analogs of MPEG or decomposition products arising from MPEG. And since purification by vacuum distillation of impure MPEG was unsuccessful, boiling point determination may also be a poor method to establish identity and purity.

Before the characterization of the column-isolated impurity was complete,  $^1\text{H}$  NMR analysis appeared to show that DMF was present, as the two methyl singlets indicated the presence of a dimethylamide. However,  $^{13}\text{C}$  NMR analysis clearly ruled the presence of DMF out, and the phthalamate structure was established by HRMS. The simplest explanation for the formation of this phthalamate envisions an acyl transfer reaction in which dimethylamine condenses with MPEG, forming methanol as a byproduct. The formation of amides from esters is favorable, and can be base catalyzed (March, **1992**). The reaction conditions used to synthesize the Incon MPEG involve excess sodium methoxide and DMF at 120 °C, and very likely generated dimethylamine; sodium hydroxide is known to appreciably decompose DMF under reflux temperatures to dimethylamine (Armarego and Chai, **2009**). With dimethylamine present, an acyl transfer reaction with MPEG would be expected to readily occur at 120 °C.

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2) The solubility of pure MPEG in *n*-hexane is approximately 10 mg/mL.



The long term stability and appropriate storage conditions of MPEG remain unanswered. For the MPEG standard that had been purified from Incon material, GC analysis did show that some decomposition had occurred. This Incon purified MPEG was not quite analytically pure at the time it was purified, and was stored in a clear glass vial with a screw-top lid. No precautions were taken against light or humidity, and the room temperature varied from 15-35 °C over that time period. Our MPEG standard will start to yellow overnight if left uncovered and exposed to air at room temperature. We strongly suspect oxygen is the culprit, as this sample was kept in the dark. Of course until MPEG aging is more fully understood, samples in the meantime should be stored in dark glass at 4 °C under Argon. The relationship between MPEG purity and its physical properties, such as density, viscosity, surface tension, boiling point, etc., also remain unclear, and many of these properties can affect propellant mixing.

## CONCLUSIONS

We have purified and characterized MPEG to be used as an analytical standard for routine GC analysis of bulk lots of MPEG. With the use of GC analysis, the minimum values of purity and other physical properties of MPEG required for acceptable propellant manufacturing can be determined. In addition, aging characteristics of MPEG and proper storage conditions can also be determined. Pure samples stored under Argon do not appear to decompose. MPEG impurities and molecular oxygen do appear to play the dominant roles in the aging characteristics and decomposition of MPEG, which may alter the physical properties of MPEG and may affect its effectiveness as a plasticizer. We have isolated a major impurity of MPEG and have characterized its structure. The formation of this impurity can be directly attributed to the specific method of synthesis of MPEG.

## EXPERIMENTAL SECTION

MPEG was procured from City Chemical (Lot 21D72) and from Incon Industries, Inc. (Lot ND/01/01). Diethyl ether (stabilized with BHT) and silica (200-400 mesh, 60Å) were purchased from Aldrich Chemical Co. Retention factors ( $R_f$ ) for thin layer chromatography (TLC) were performed using Sigma-Aldrich 0.20 mm silica gel pre-coated aluminum plates; spots were visualized under UV light. Distillation glassware, including a vacuum-jacketed short-path distillation head, were oven dried for >2 h at 120 °C.

$^1\text{H}$  and  $^{13}\text{C}$  NMR analyses (300.1 and 75.5, respectively) were performed on an Agilent DD2 300 instrument in samples dissolved in  $d_6$ -DMSO at 25.0 °C ( $\pm 0.1$  °C). Downfield chemical shifts are recorded in positive  $\delta$  units in ppm relative to TMS ( $\delta = 0.00$ ) for  $^1\text{H}$  NMR and to the residual solvent peak in  $d_6$ -DMSO ( $\delta = 39.43$ ) for  $^{13}\text{C}$  NMR. Proton decoupling (WALTZ-16) was used for acquiring the  $^{13}\text{C}$  NMR spectra. A matched exponential filter (line broadening = 0.3 Hz) was used for processing the  $^{13}\text{C}$  NMR spectra, and the digital resolution was 0.07 Hz/data point. Multiplicities are described as singlet

(s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of doublet of doublets (ddd), multiplet (m), and broad (br). IR spectra were recorded on a Thermo Nicolet Avatar 370 Fourier transform infrared spectrometer at 2 wavenumber resolution using a Germanium ATR accessory. UV-Vis spectra were recorded on a Varian Cary 100 Bio UV-Vis spectrometer. High resolution (<10 ppm) mass spectra were obtained on a JEOL AccuTOF (time-of-flight) mass spectrometer under DART ionization conditions (250 °C, 20 eV), calibrated to PEG 600. GC analysis was performed on duplicate samples according to ASTM method D3465, using a Hewlett-Packard 5890 Series II with a J&W DB-5 capillary column (length = 30 m, inside diameter = 0.25 mm, film thickness = 0.25  $\mu$ m) with He as the carrier gas (1 mL/min), and a temperature profile of 10 °C/min from 100 °C to 300 °C and then held for 10 min. GC-MS spectra were obtained on an Agilent 7890A GC using a Restek Rtx-5MS capillary column, with the same column dimensions and temperature profile as the GC, and on an Agilent 5975C MSD (quadrupole) mass spectrometer under electron ionization conditions (200 °C, 70 eV); peak abundances of the mass-to-charge ratios ( $m/z$ ) are reported as a relative percent of the base peak (100%). Boiling points are uncorrected. Elemental analysis (<0.4%, triplicate samples) and Karl Fischer (single sample) analysis were performed by Galbraith Laboratories, Inc. Relevant spectra are included in the Supporting Information section.

A solution of City Chemical MPEG (1.00 g) in Et<sub>2</sub>O was loaded onto silica gel column (dry height = 25 cm, diameter = 2.2 cm) prepared using 45 g silica and 200 mL Et<sub>2</sub>O. Flash column-chromatography using 200 mL of Et<sub>2</sub>O eluted MPEG (0.98 g). TLC showed one spot,  $R_f$  = 0.63 (Et<sub>2</sub>O). The MPEG solution in Et<sub>2</sub>O was dried over sodium sulfate, stirring overnight (ca. 16 h) at room temperature, and then vacuum-filtered (Whatman #1) via a dry pump. After the solvent was removed by short-path distillation, the flask was placed under high vacuum and gentle heating from a heat gun removed the final traces of solvent. The flask was then kept under high vacuum (<0.01 Torr) for 4 more hours. This MPEG standard was stored at 4 °C under Ar.

The Incon MPEG was first vacuum-filtered via water aspiration using Whatman #1 filter paper (d = 4.25 cm) over 2 h, isolating MPEG as a viscous, yellow liquid (115 g) and a white, wet solid (12 g) as the filtered precipitate. The wet solid re-solidified to a waxy solid after a mild heating-cooling cycle. Flash column-chromatography was performed on the vacuum-filtered MPEG (4 g) using silica gel and Et<sub>2</sub>O as described above, yielding MPEG (3.7 g) in high purity, and the major impurity,  $R_f$  = 0.12 (Et<sub>2</sub>O), was isolated using an ethyl acetate gradient. This MPEG solution was not dried, and the oil was concentrated to dryness using rotary evaporation via a water aspirator pump, and then placed on a high-vacuum pump. This not quite analytically pure MPEG was stored at room temperature in a clear glass vial with a screw-top lid.

Successful vacuum distillation of 1 g of our MPEG standard was conducted using a 5-mL round bottom flask with a stir bar. The contents of the flask were heated to 255 °C under vacuum at 0.10 Torr, to yield MPEG whose purity remained unchanged by <sup>1</sup>H NMR analysis. The distillate and the distillation flask contents both remained colorless. An unsuccessful vacuum distillation was attempted on 50 g of the vacuum-filtered Incon MPEG. Boiling chips were added, and the contents of the 100-mL round bottom flask were heated to 255 °C under vacuum between 0.25 and 1 Torr. The vacuum distillation was unsuccessful, and the contents of the distillation flask had turned to a dark red liquid.

Using a separatory funnel, a solution of vacuum-filtered Incon MPEG (29.4 g) in Et<sub>2</sub>O (75 mL) was washed with concentrated (0.85 M) sodium bicarbonate (5 x 35 mL), water (2 x 25 mL), and saturated brine (1 x 25 mL). After drying with MgSO<sub>4</sub>, the oil was concentrated to dryness using rotary evaporation via a water aspirator pump, and then placed on a high-vacuum pump, to yield impure MPEG (25.7 g) by TLC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR analyses. Next, a methylene chloride (75 mL) solution of this treated MPEG (25.2 g) was washed with saturated (1.2 M) sodium bicarbonate (8 x 25 mL), water (3 x 25 mL), and saturated brine (1 x 25 mL). After drying with MgSO<sub>4</sub>, the oil was concentrated to dryness via rotary evaporation, and then placed on a high-vacuum pump, to again yield impure MPEG (23.5 g) by TLC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR analyses. Last, a methylene chloride (50 mL) solution of this twice treated MPEG (23.1 g) was washed with concentrated (2 M) sodium carbonate (4 x 100 mL, allowed to sit for 5 min before separating), water (2 x 100 mL), and saturated brine (1 x 100 mL). After drying with MgSO<sub>4</sub>, the oil was concentrated to dryness via rotary evaporation, and then placed on a high-vacuum pump to yield impure MPEG (16.8 g) by TLC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR analyses.

#### **Methyl phthalyl ethyl glycolate (MPEG) [85-71-2]**

bp: 137 °C (0.10 Torr)

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ 7.84-7.71 (m, 4H), 4.90 (s, 2H), 4.19 (q, 7.1Hz, 2H), 3.81 (s, 3H), and 1.23 (t, 7.1Hz, 3H) ppm.

<sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ 167.3, 167.2, 166.0, 132.2, 131.9, 131.5, 130.0, 128.9, 128.7, 61.6, 60.9, 52.5, and 13.9 ppm.

IR (ATR): 1728, 1598, 1580, 1434, 1380, 1360, 1286, 1210, 1124, 1080, 1034, and 960 cm<sup>-1</sup>.

UV-Vis (EtOH): λ<sub>max</sub> 272 nm (ε = 1.8 x 10<sup>4</sup>).

GC: 99.5 ± 0.1%

GC-MS: *m/z* 266 (5, M<sup>+</sup>), 235 (15), 163 (100), 149 (10), and 77 (15).

HRMS: Calcd for C<sub>13</sub>H<sub>15</sub>O<sub>6</sub> [M+H]<sup>+</sup> 267.0863. Found 267.0866 (1.1 ppm).

Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>6</sub>: C, 58.65; H, 5.30; O, 36.05. Found: C, 58.33; H, 5.27; O, 36.22.

KF: H<sub>2</sub>O <0.295%

**Ethyl glycolyl *N,N*-dimethylphthalamate**

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ 8.01 (ddd, 7.8Hz, 1.3Hz, 0.4Hz, 1H), 7.73 (dt, 7.5Hz, 1.4Hz, 1H), 7.58 (dt, 7.7Hz, 1.4Hz, 1H), 7.36 (ddd, 7.6Hz, 1.3Hz, 0.4Hz, 1H), 4.88 (s, 2H), 4.17 (q, 7.1Hz, 2H), 2.96 (s, 3H), 2.69 (s, 3H) and 1.21 (t, 7.1Hz, 3H,) ppm.

<sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ 169.2, 167.4, 164.5, 139.2, 133.6, 130.0, 128.8, 127.0, 125.6, 61.4, 60.9, 37.7, 34.0, and 13.9 ppm.

IR (ATR): 2958, 2930, 1726, 1638, 1602, 1400, 1276, 1212, 1132, 1074, and 1040 cm<sup>-1</sup>.

HRMS: Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>1</sub>O<sub>5</sub> [M+H]<sup>+</sup> 280.1180. Found 280.1193 (4.6 ppm).

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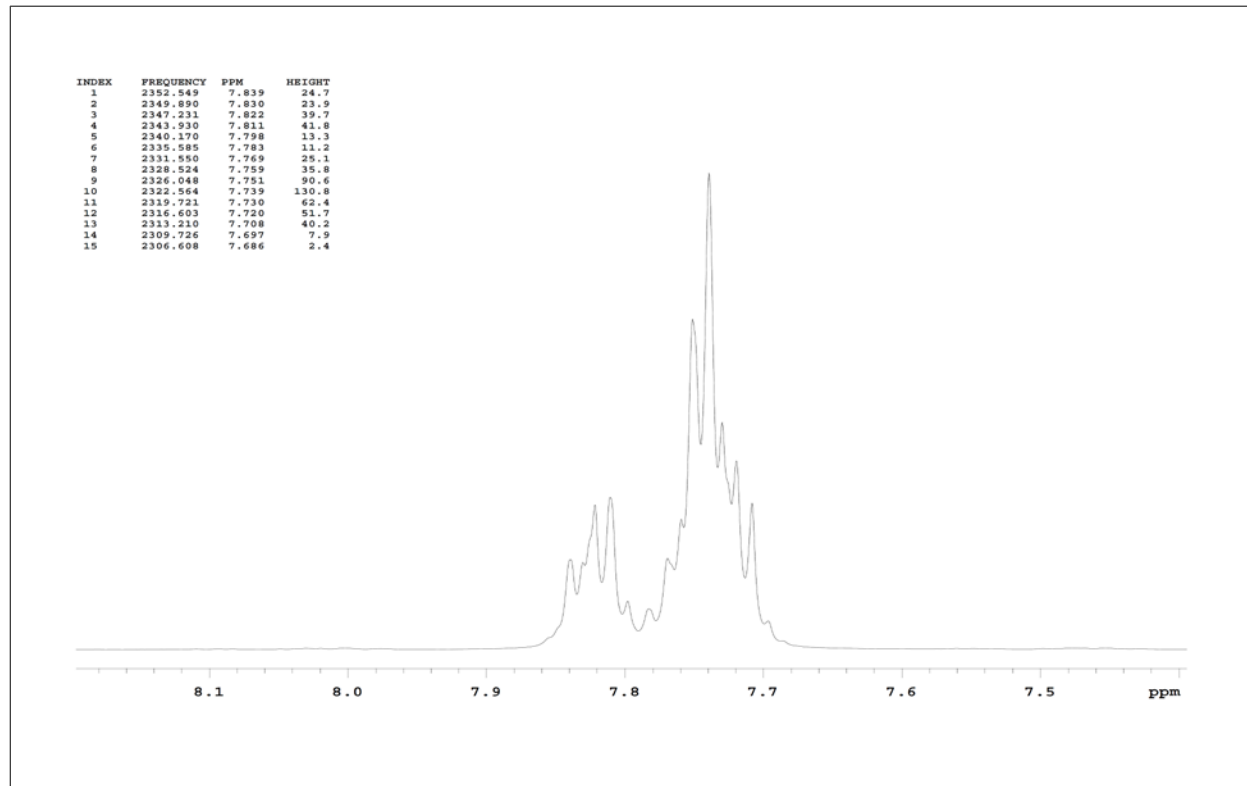
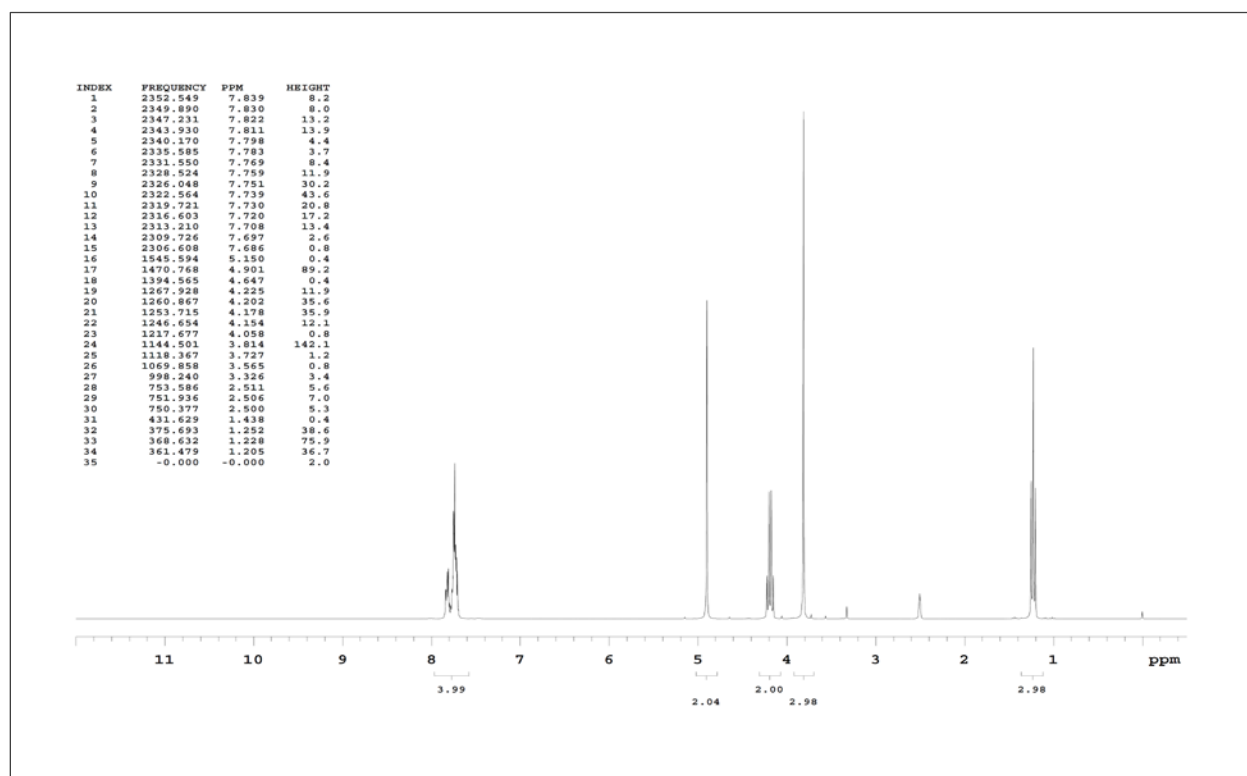
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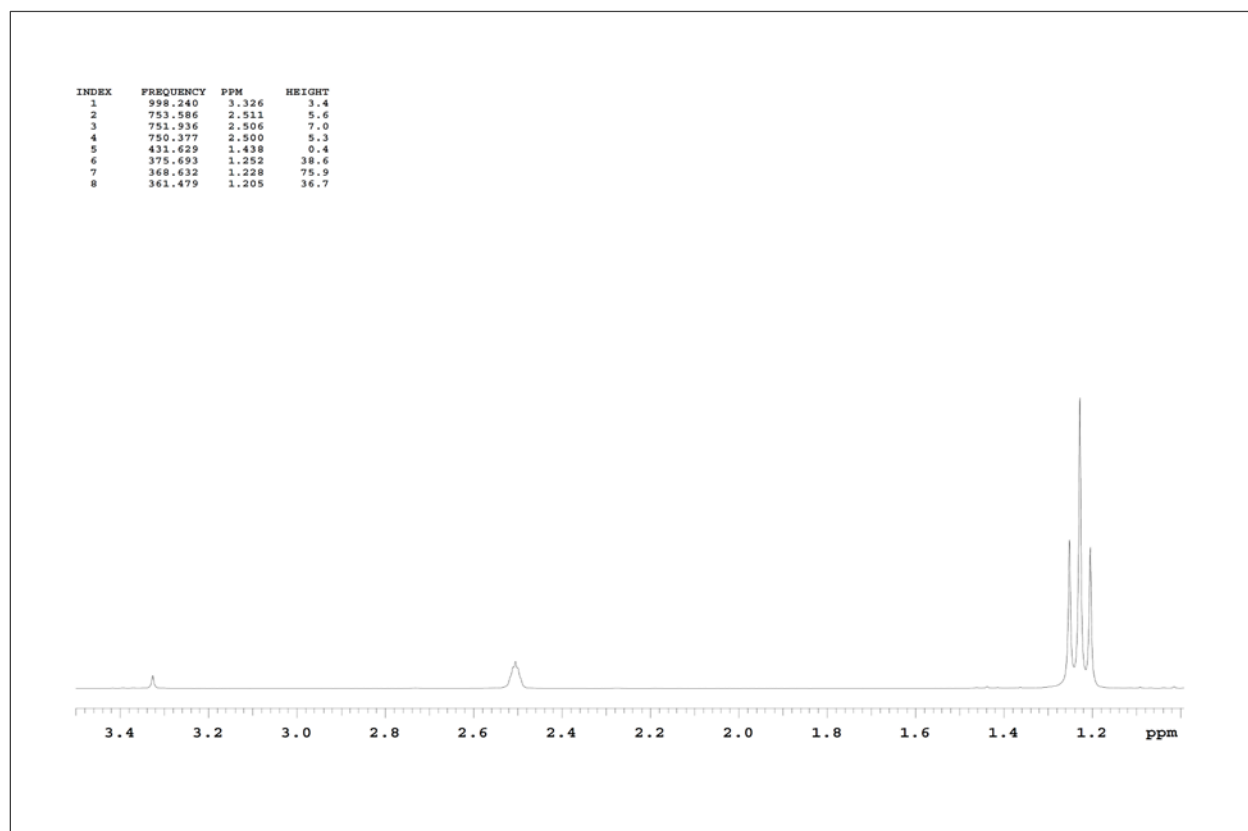
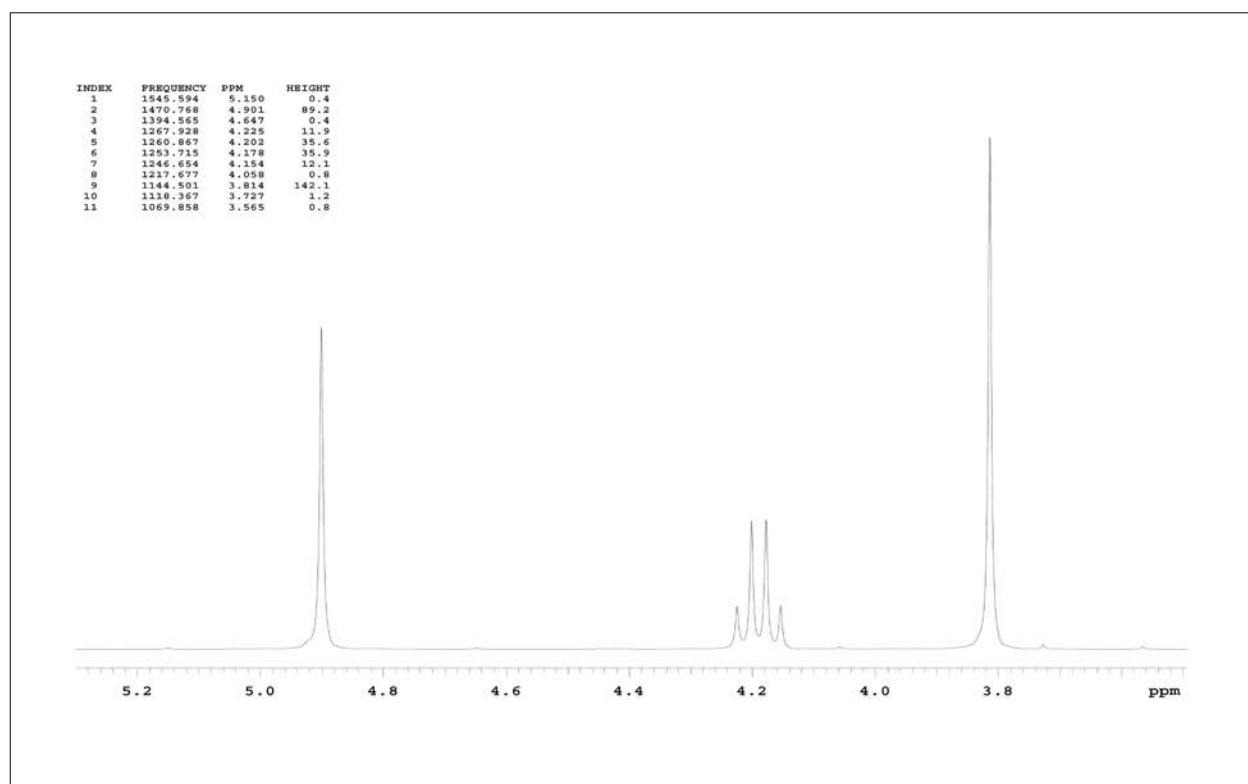
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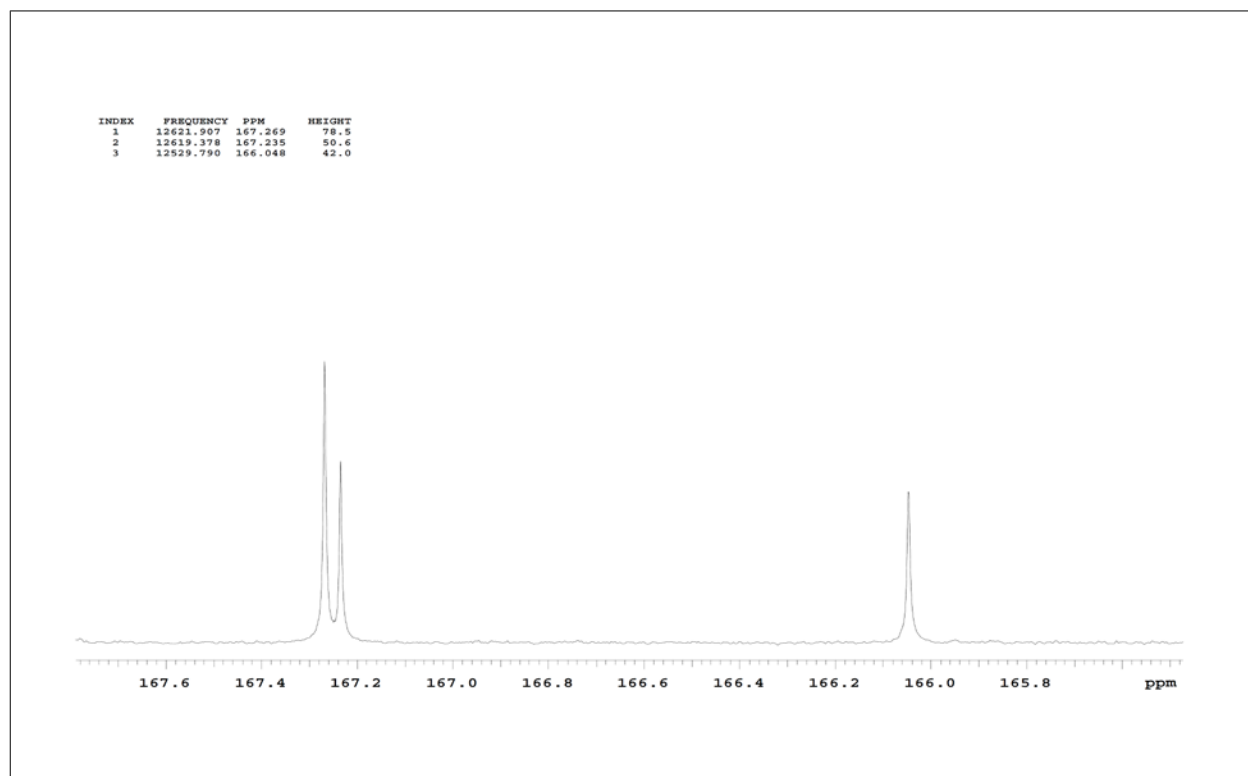
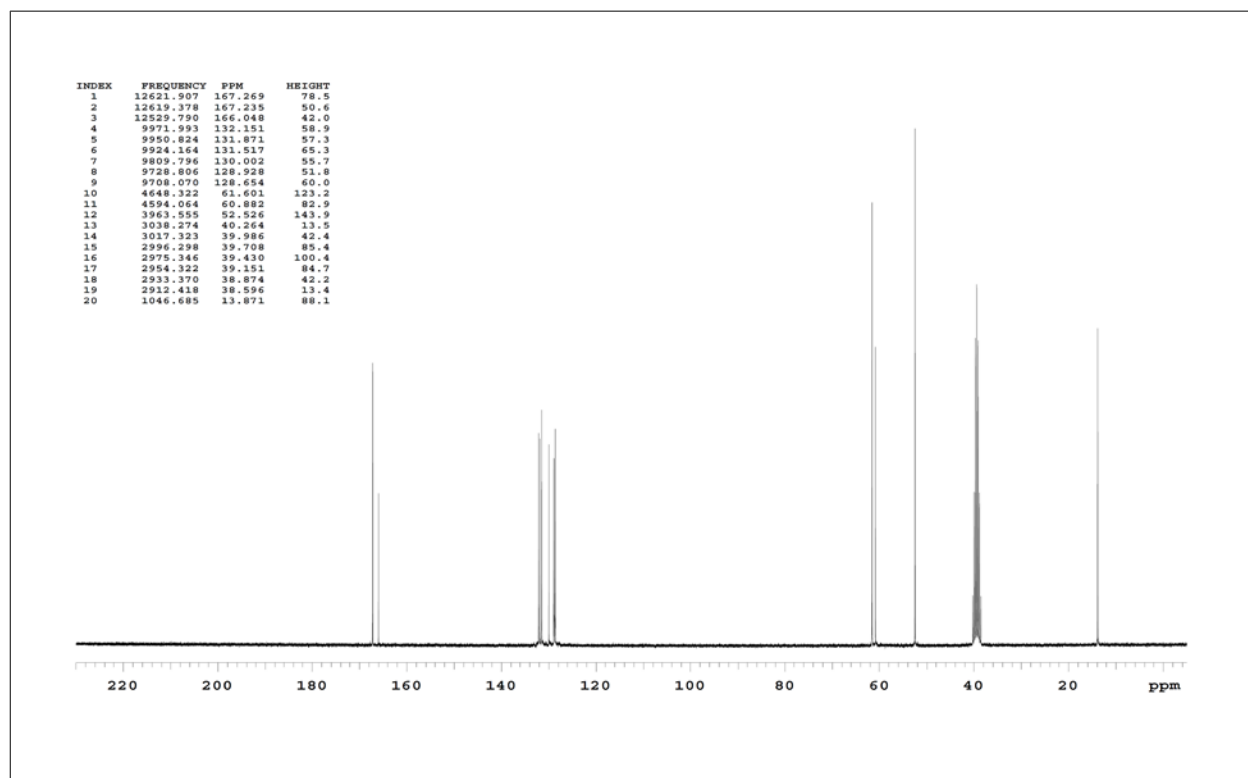
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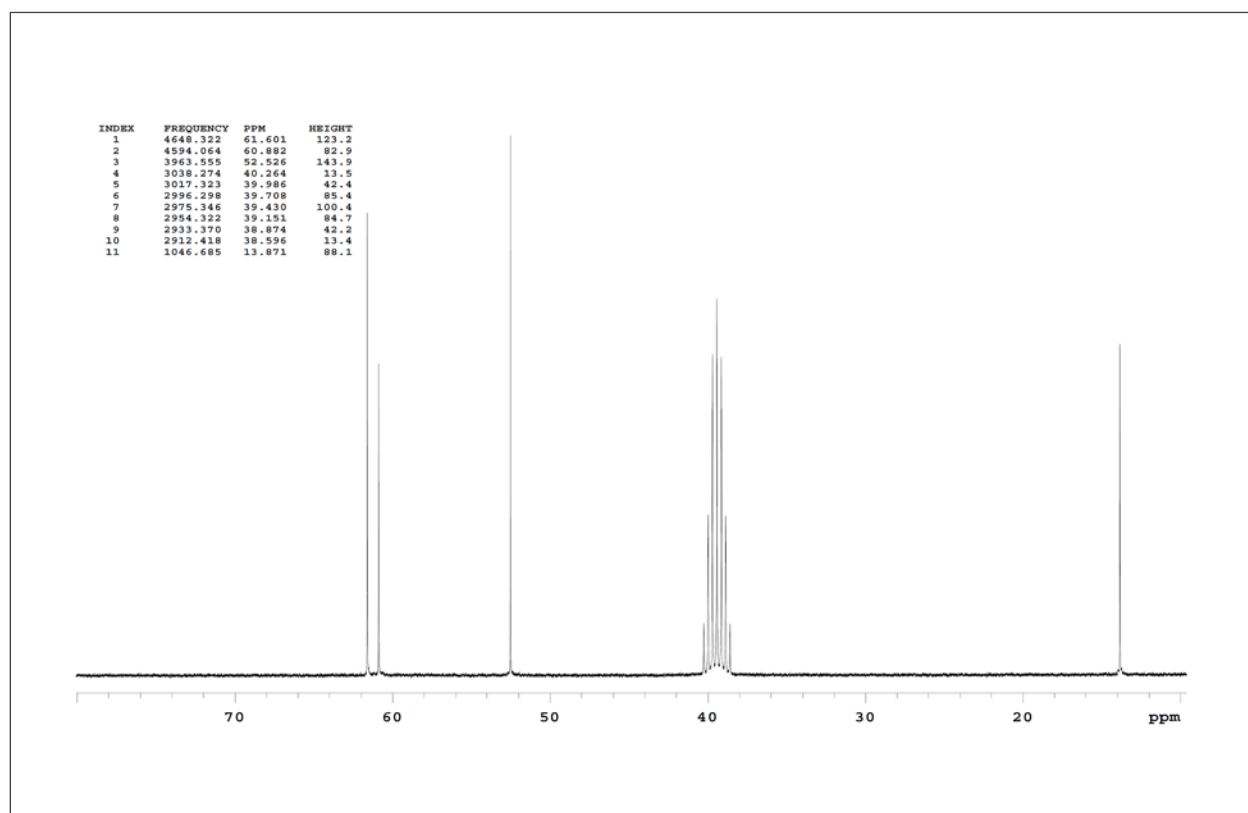
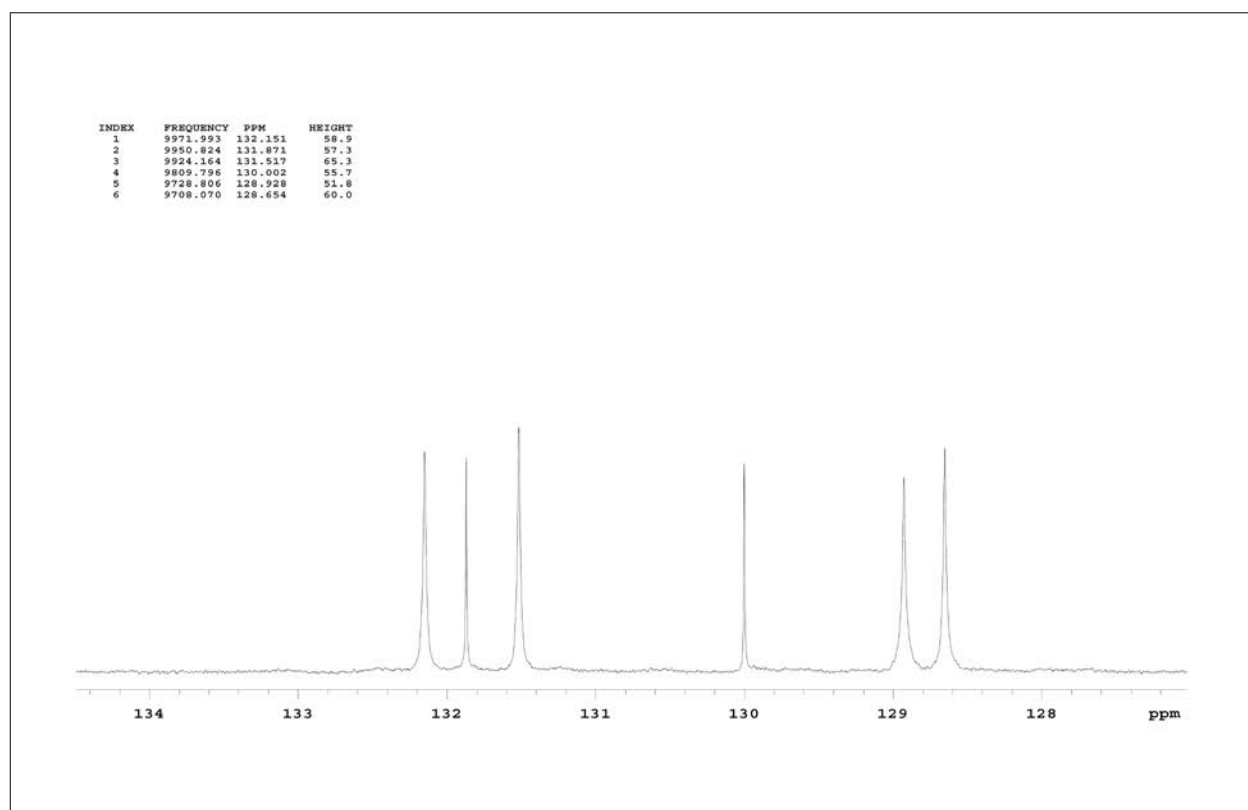
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<sup>13</sup> C NMR	16
IR	18
HRMS	18
GC	19
GC-MS	19

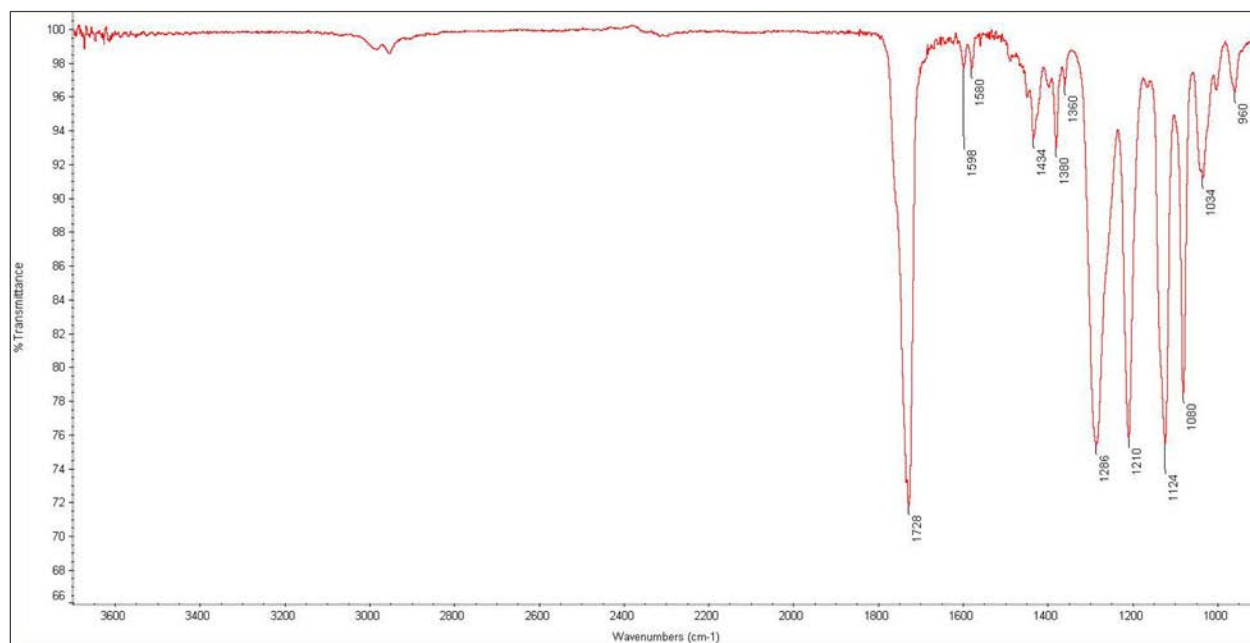
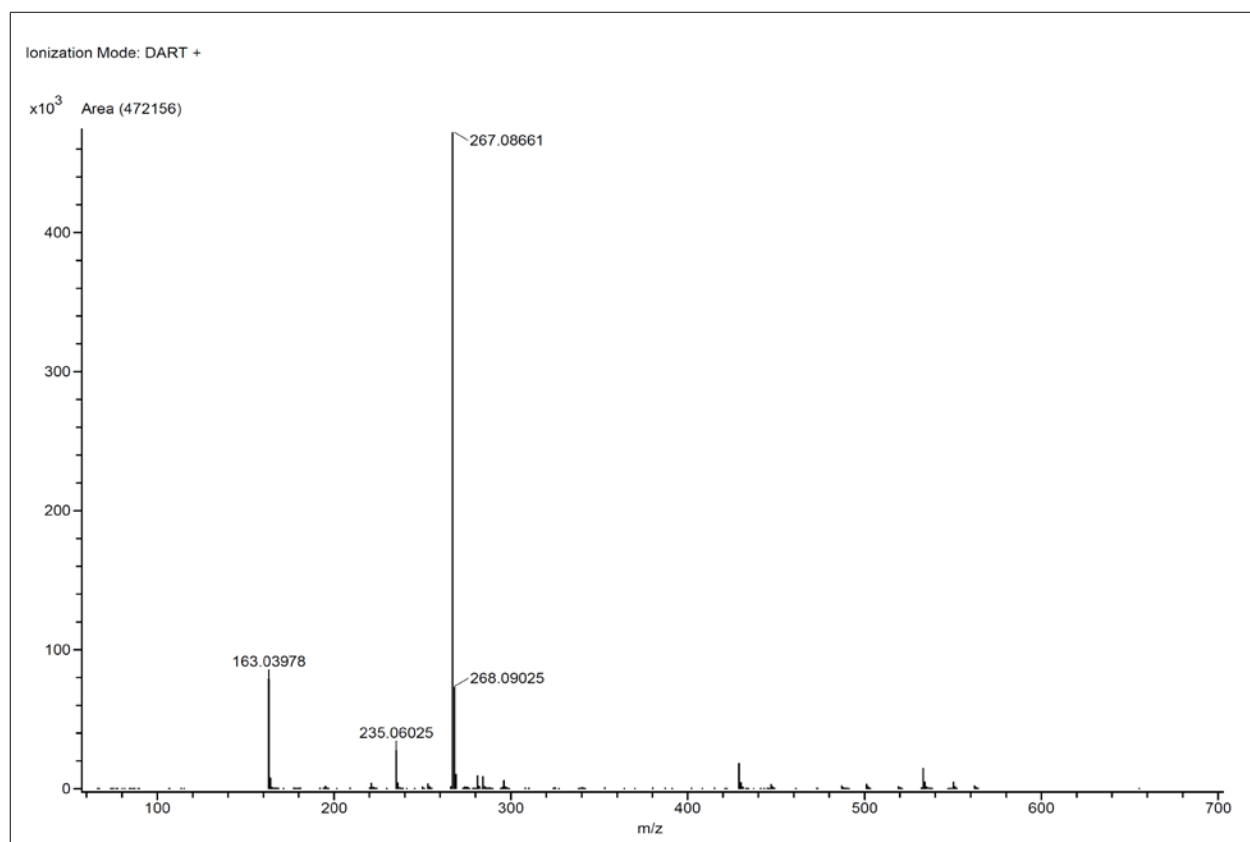
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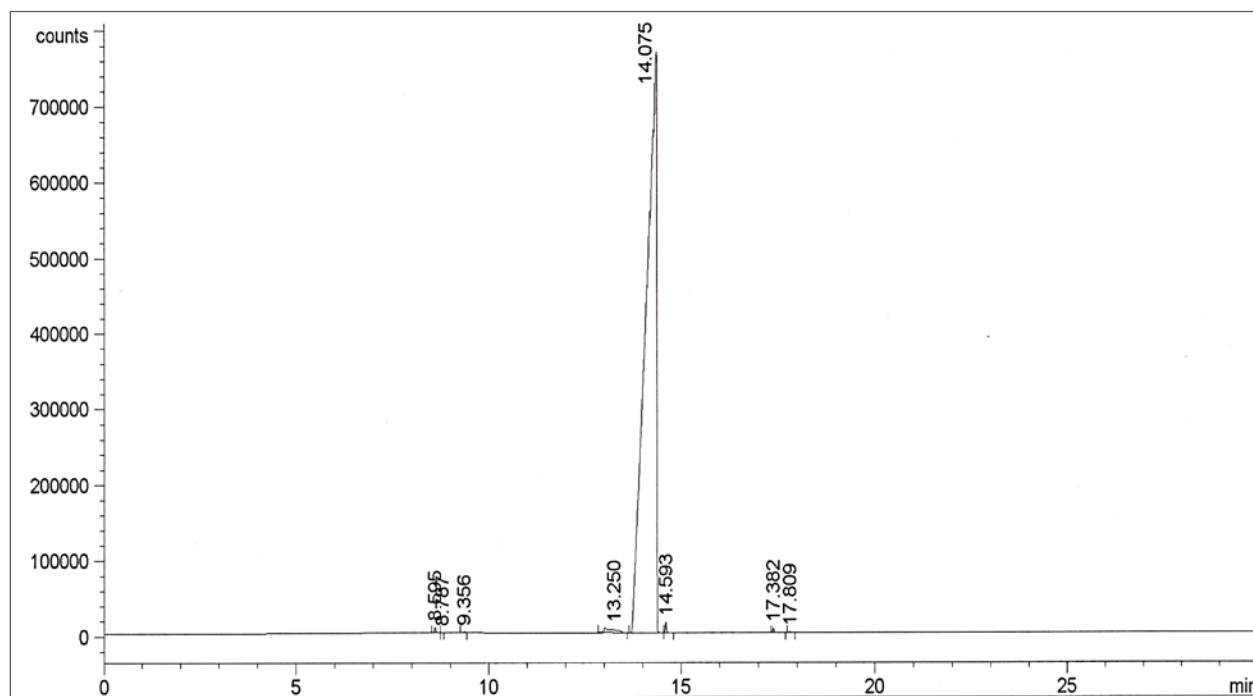
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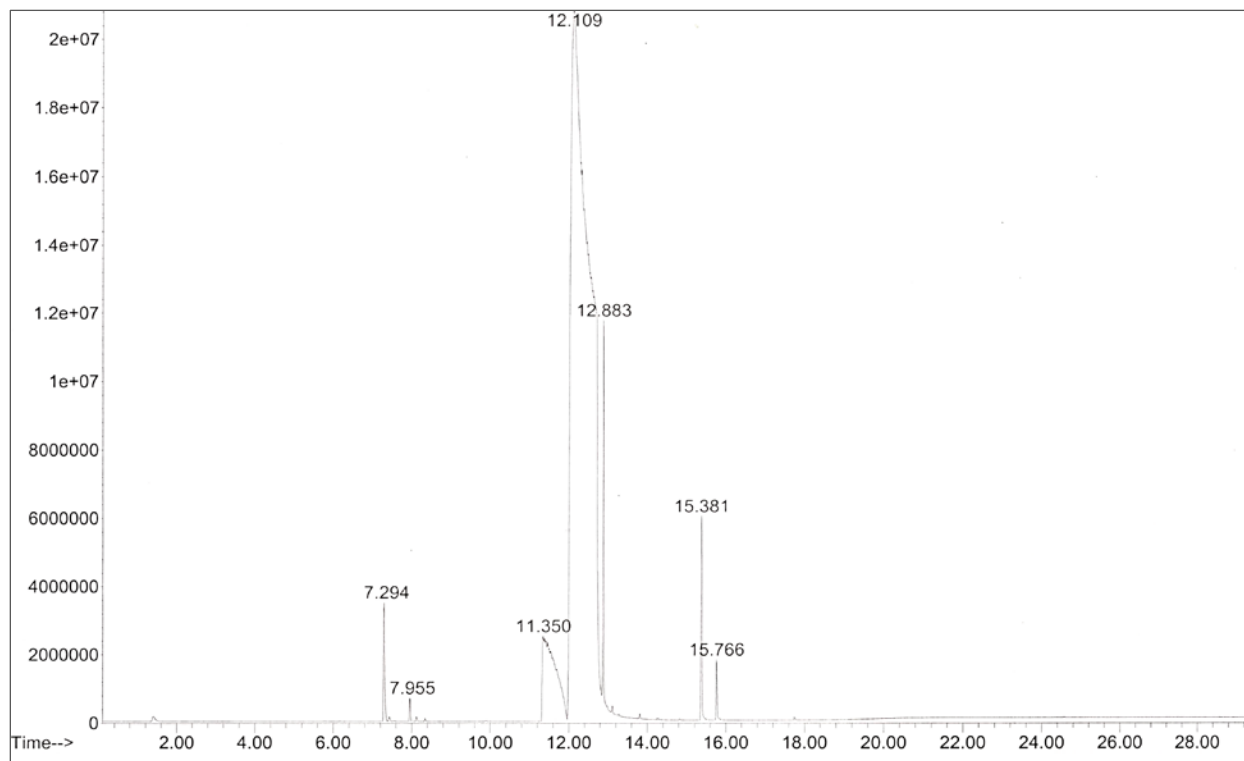


**MPEG / IR****MPEG / HRMS**

## MPEG / GC



## MPEG / GC-MS



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